Use of Novel Surfaces to Reduce Bioadhesion on Infrastructure

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Standard Form 298 (Rev. 8-98)
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Overview

- Research context: DoD relevance
- Recent technology history
- Novel surface properties employed
- Methods
  - Material science
  - Biological
- Bioadhesion resistance efficacy
- Conclusions
- Future Directions

Research context: DoD relevance

- <u>Problem</u>: invasive species stowaways
  - Snails, plant propagules, microbes
  - Biodiversity and agricultural
- Current solution
  - Executive Order 13112
  - Army Forces Washdown Guidance
  - Chemical control: methaldehyde
  - Physical inspection / removal

Armed Forces Pest Management Board

Technical Guide No. 31

RETROGRADE WASHDOWNS:

Cleaning and Inspection Procedures

Published and Distributed by the
EST MANAGEMENT INFORMATION ANALYSIS CENTER
Forest Glen Section
Walter Reed Army Medical Center
Washington, DC 20307-5001
November 2004

Table 6. Estimated cost for vehicle cleaning in Kuwait.

(Assume labor cost of $5-10/hr and 2 persons per vehicle)

Month	Total Vehicle Cleaning Time, hr	Labor Cost, 2 Pers @ $5/hr	Labor Cost, 2 Pers @ $10/hr
Nov	14,322	$143,220	$286,440
Dec	10,465	$104,650	$209,300
Jan	50,175	$501,750	$1,003,500
Feb	84,502	$845,020	$1,690,040
Mar	179,784	$1,797,840	$3,595,680
Apr	69,894	$698,940	$1,397,880
May	17,116	$171,160	$342,320
Jun	7,333	$73,330	$146,660
Jul	47,043	$470,430	$940,860
Total (9 months)	480,634	$4,806,340	$9,612,680

CoFrancesco et al. TR-07-8 (2007)
Natural Selections volume 6, issue 2 (2010)

Model species selection

- Terrestrial gastropod
  - Danger to crops
  - Intermediate host to pathogens
  - Nocturnal – vehicles parked

Scientific Name	Number of Interceptions	Countries of Origin
Theba pisana	376	Spain-Israel-Portugal
Helicella spp	307	Italy-Israel-Greece
Helix aspera	192	Italy-Mexico-Spain
Succinea horticola	146	Italy-Japan-Greece
Helicella conspurcata	119	Italy-Spain-Greece
Cochlicella barbara	109	Italy-Spain-Greece
Cochlicella spp	108	Israel-Portugal-Italy
Monacha spp	54	Israel-Italy-Greece
Helicella maritima	53	Italy-Spain-France
Monacha syrlaca	48	Greece-Italy-Turkey
Helicella cretica	48	Greece-Italy-Turkey
Helicella virgata	47	Italy-Spain-France
Monacha carthusiana	47	Italy-France-Israel
Helicella gigaxii	46	Italy-Spain-Greece
Otala spp	45	Italy-Greece-Spain
Cepaea spp.	42	Hawaii-Brazil-France
Cochlicella conoidea	35	Italy-Germany
Helicella protea	31	Turkey-Italy-Israel
Achatina fulica	31	Hawaii-Taiwan-Hong Kong
Helicella derbentina	28	Turkey-Italy-Greece

Source: Interception Records (1974-1987) USDA-APHIS

- Biofilm forming bacteria
  - Disease transfer
  - Troop respiratory and urinary infections in hospitals


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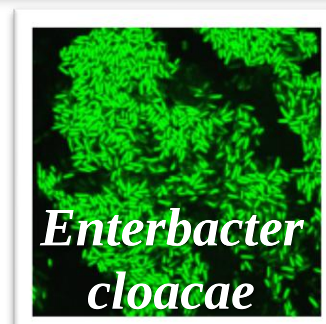
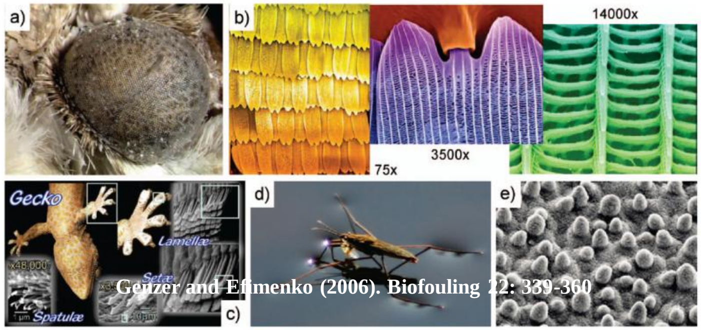


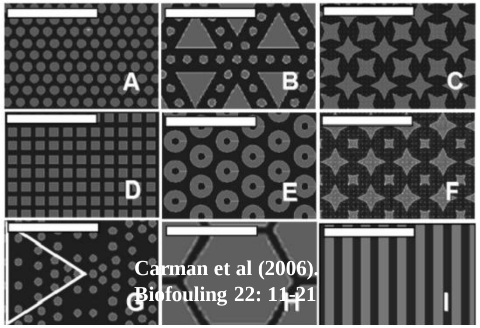
Rationale: Environmentally benign surfaces

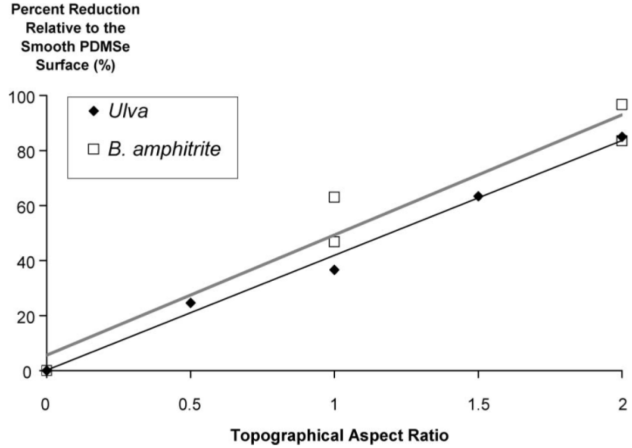
- Chemical / physical controls undesirable
  - Bottom paints: copper, TBT
  - Non-target species, legacy contamination
  - Laborious
- <u>Bio-inspiration</u>: leverage biological surfaces that have adapted unique properties
  - Adapted over 1000s of years
- <u>Hypothesis</u>: microstructured pattern tessellations, hydrophobicity, surface properties or hybridizations will reduce bioadhesion via:
  - Behavioral cues (lack of surface recognition)
  - Mechanistic properties (compromised adhesion or micro-fluid layer interfacial interactions



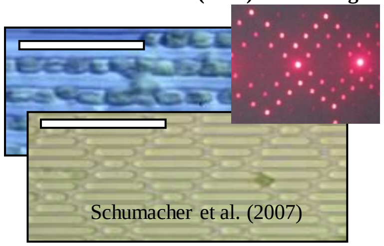
Background: Textured surfaces

- Leverage hierarchical structures on biological surfaces
- Surface feature height and aspect ratio affects bioadhesion
- Sharklet® technology: Navy
- Greater than 80% reduction in *Ulva* spore and barnacle adhesion
- Not investigated for terrestrial systems





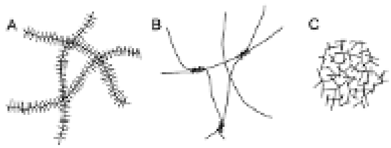
Schumacher et al (2007). Biofouling



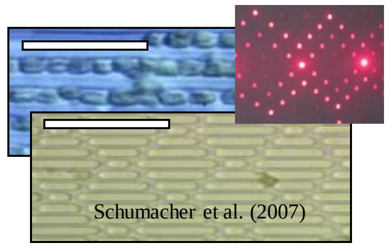
Surface properties and the bio-interface

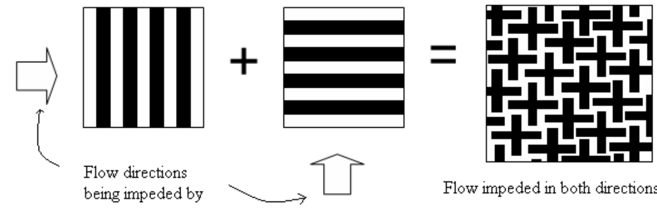
Novel strategy		Parameters	Description
1	Mechanical	Elastic modulus Hardness	Ability to return to original dimensions after deformation
2	Hydrodynamic	Surface pattern, Dimension, roughness	Patterns of microsized dimensions
		Hydrophobic	Water fearing surface
		Hydrophilic	Water loving surface
3	Chemical	Biocide release pH, ionic strength	Toxic / aversion to model species

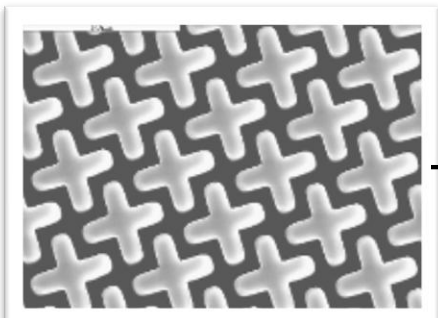
Greater elasticity →	PDMSe Teflon Cross pattern Screen pattern →	Dry mucus seal fails due to cavitation / cracking
Lower surface energy →	Teflon PDMSe Cross pattern →	Insufficient mucus spreading or phase separation
Lesser surface area for contract →	Cross pattern Screen pattern →	Less area available for gluing



Methods: Topographical surfaces

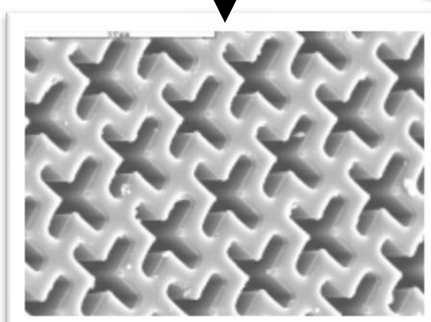






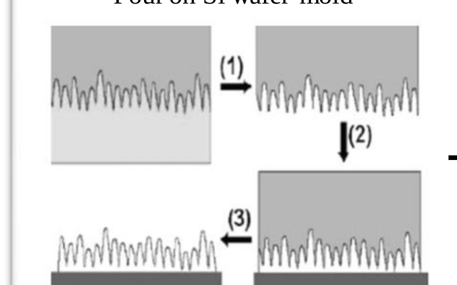
Concept

photolithography



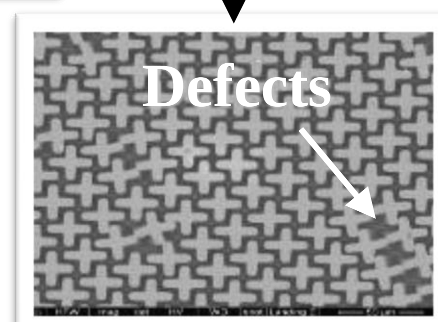
Mask: Si wafer

Silastic T2 polydimethyl siloxane resin + polymethyl silane curing agent, mix, degas to remove bubbles



Macromol. Rapid Commun. 2006, 27, 1859–1864

Peel off PDMSe



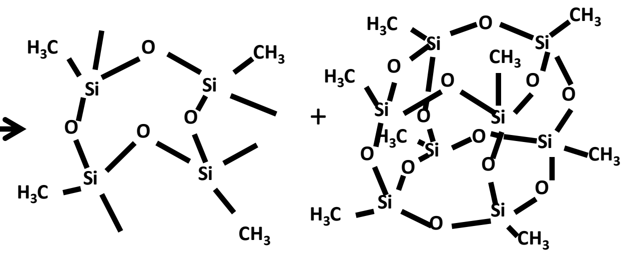
Methods: superhydrophobic surface

Hydrolysis: catalyzed by oxalic acid[1]

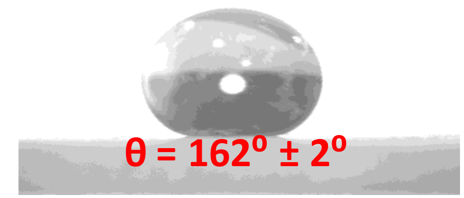
$$H_3C\text{-}Si(OCH_3)_3 + 3H_2O \xrightarrow{H_2C_2O_4} H_3CSi(OH)_3 + 3CH_3OH$$

Condensation: catalyzed by ammonium hydroxide[1]

$$n(H_3CSi(OH)_3) \xrightarrow{NH_4OH}$$



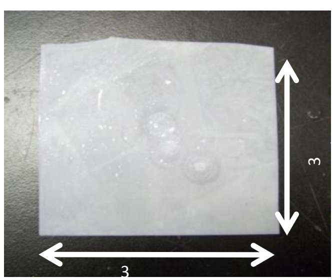
Sheet/ladder type silsesquioxane[2] + Cage type silsesquioxane[2]



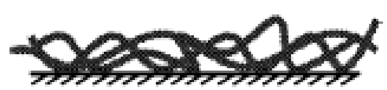
Sessile Drop Contact Angle with De-ionized water (16MΩ)

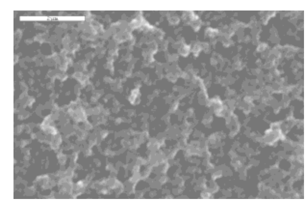
Piranha treatment: silicon wafer and glass substrates to be coated, were boiled for 10 minutes in a 1:1 solution by volume of 50% H_2O_2 and 96% H_2SO_4

Drying: The gel while in contact with the substrate is dried at 60°C for a day

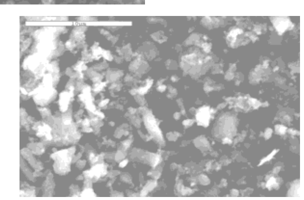


Silicon wafer coated with the 3D polymerized MTMS based sol-gel. Relatively large coated area.





A



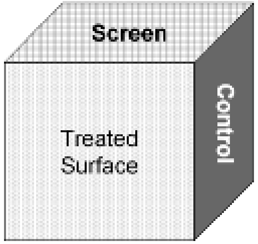
B

SEM Images A & B were taken at 15000X (SB: 2µm) and 4000X (SB: 10µm) magnifications

Methods: bioadhesion testing

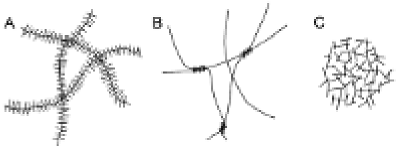
1. Real time surface interface communication
   - May be important for surface selection
   - Short-term (8-10 min) behavioral trials
   - Noldus EthoVision® digital image tracking

2. Longer-term behavior
   - Aestivation surface selection (48-h)



3. Bioadhesion
   - Whole snail
     - Shear force for removal
     - Mark-10 digital force meter
   - Fluid tensile strength
     - Mucus interaction with surface
     - Mark-10 digital force meter / test stand

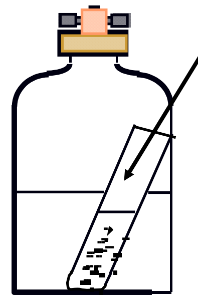
ASTM D 5618-94



$$Pascal = \frac{F}{A} = \frac{Newtons}{1/4\pi \bullet d_a^{\,2}}$$

Methods: biofilm testing

Enterobacter cloacae (-)
Grown overnight in Nutrient broth from a colony



Slide with biofilm developing

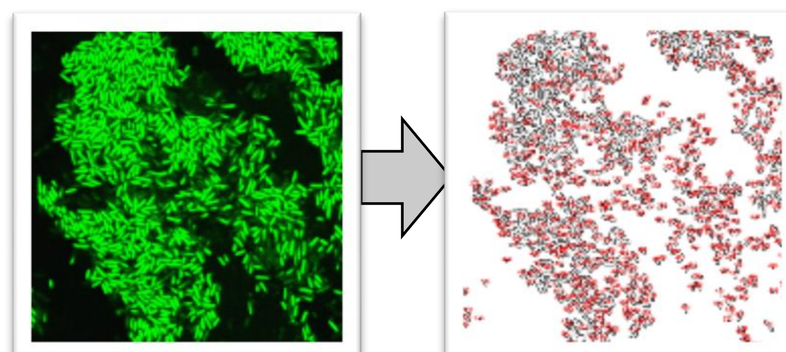
48 h Nutrient broth incubation in the presence of surface slide

Remove slide and stain

Extent of coverage assessment
1. Confocal microscopy
2. Qualitative: +/- biofilm growth
3. Quantitative: % area covered
   - Image J

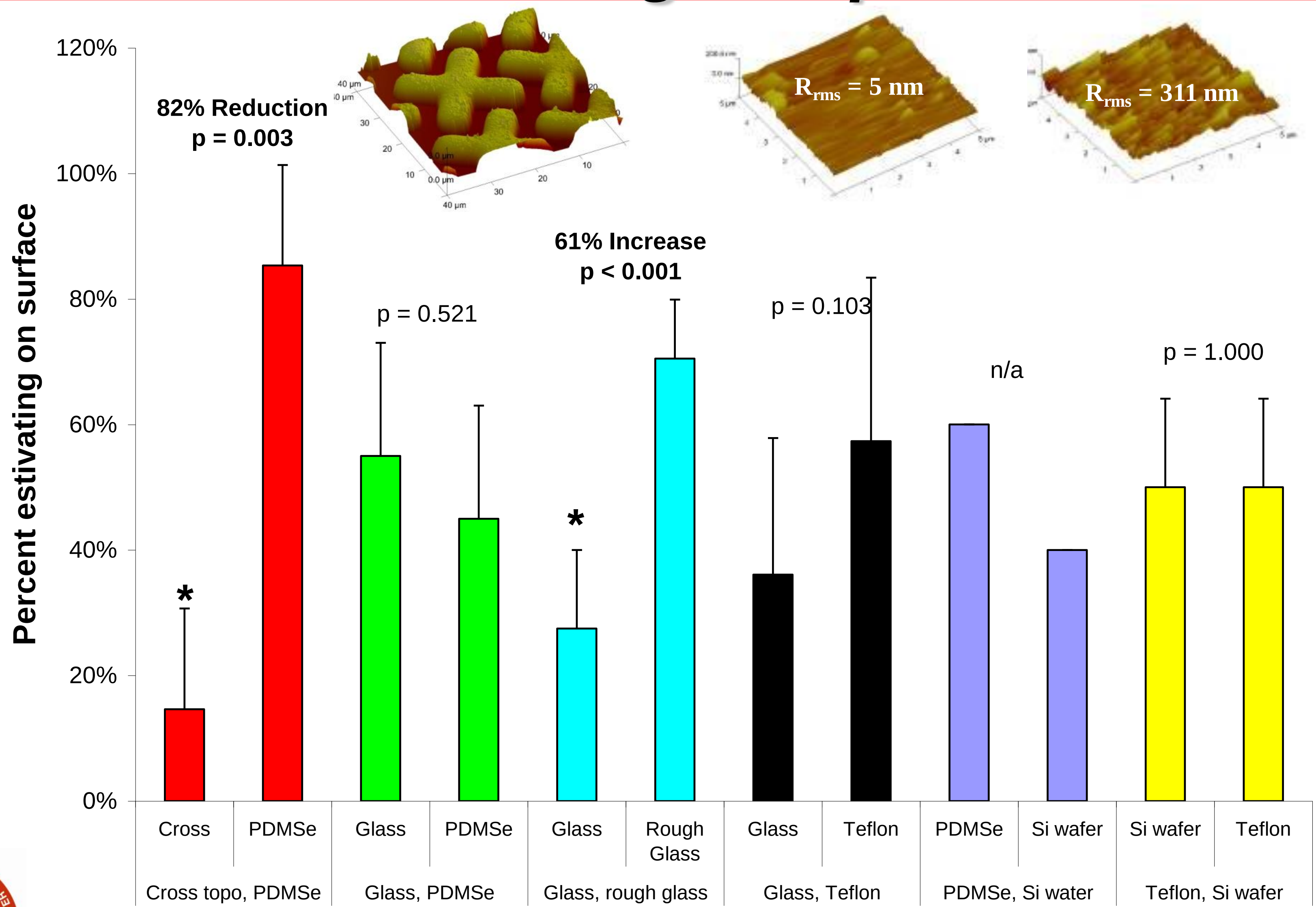
Biofilm of *Enterobacter cloacae* after 48 h incubation at 22°C

Glass surface



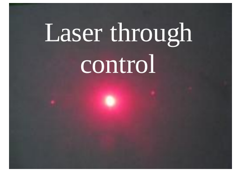
Enterobacter cloacae is associated with respiratory and urinary tract infections in hospitals increasing and has exhibited multi-drug resistance. Has use in explosives biodegradation.

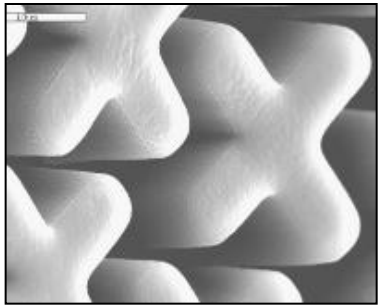
Surface selection bioadhesion: gastropod aestivation

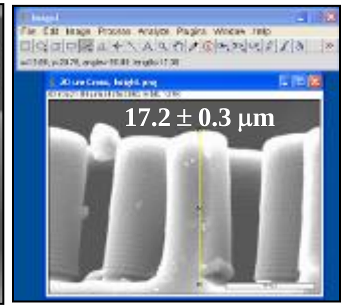


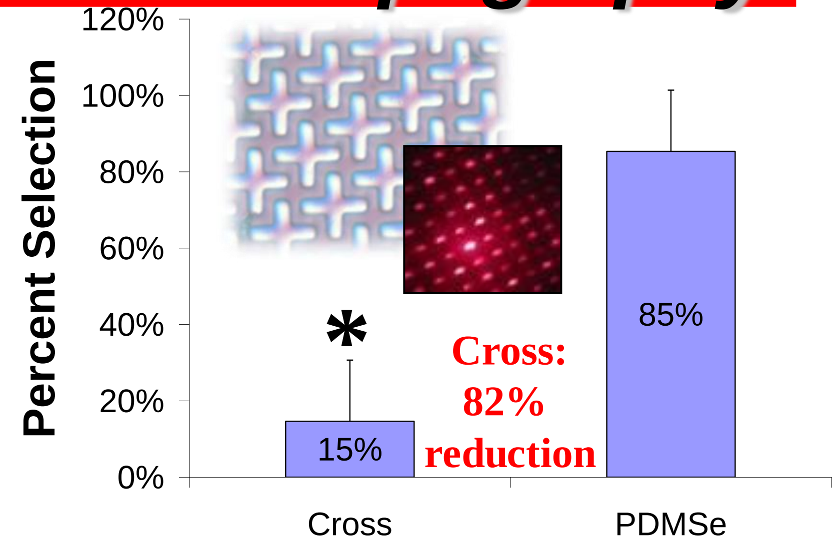
Gastropod surface selection: aestivation on cross topography

- **25 µm cross**
  - **20 µm amplitude**

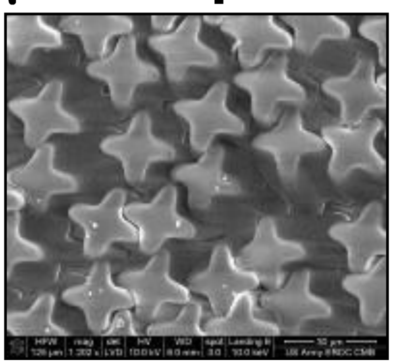


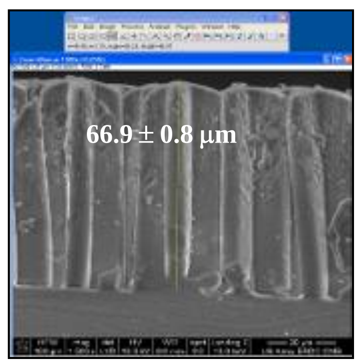


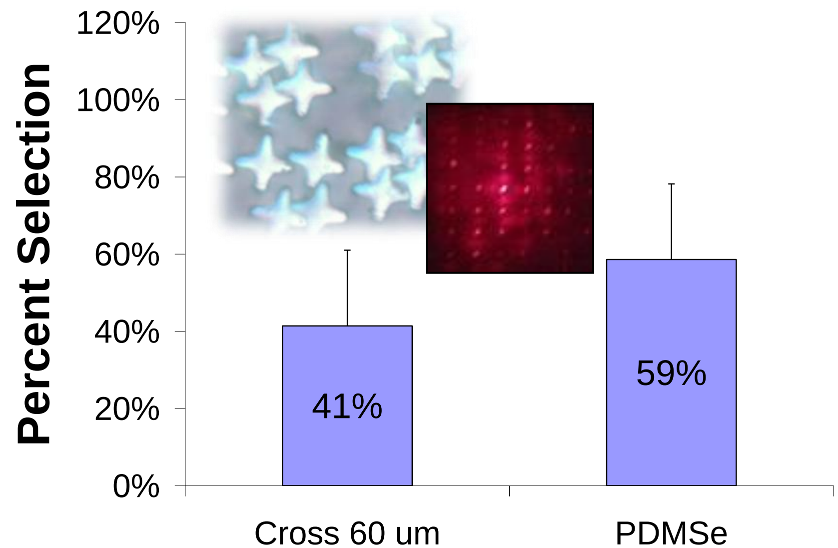




  - **60 µm amplitude (clumped)**

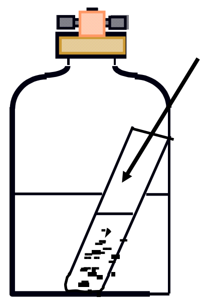


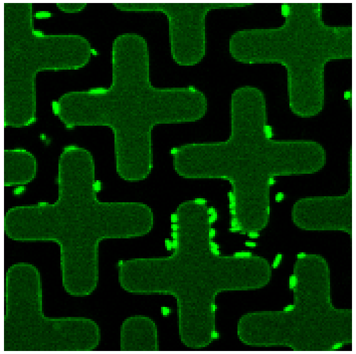


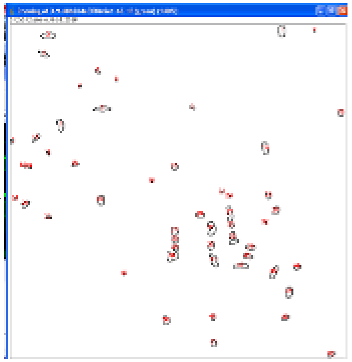


    – **Significance removed by sample reuse.**

Biofilm bioadhesion: cross topography

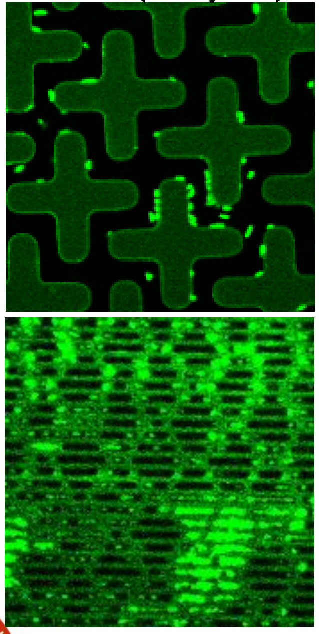


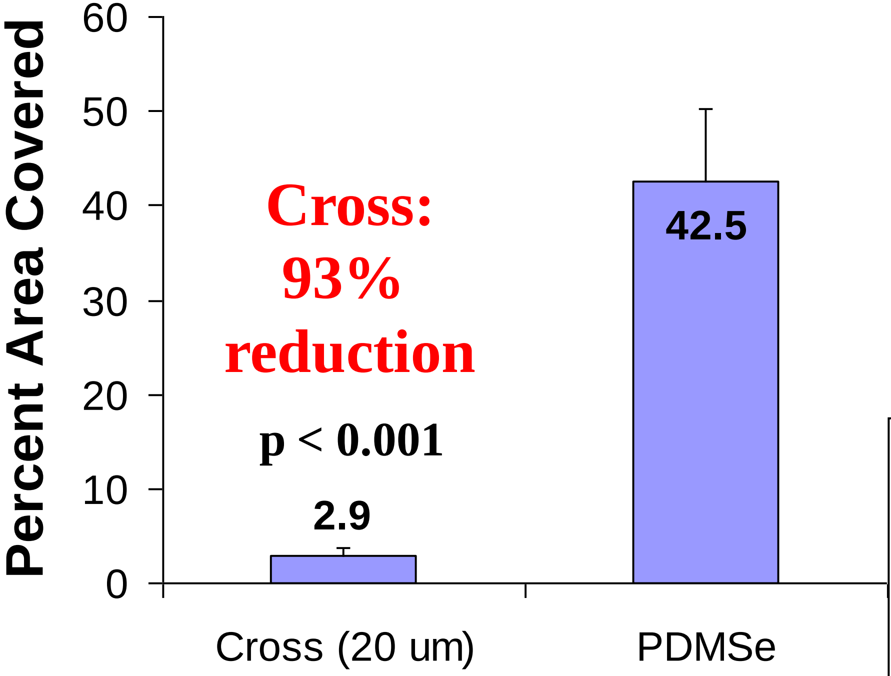




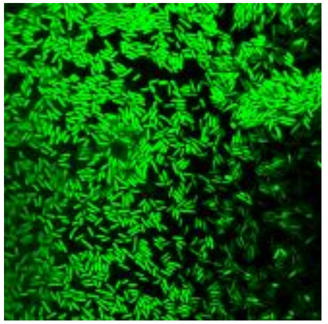
1.4% of total area covered

Cross (20 µm)





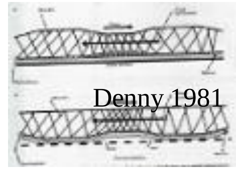
PDMSe



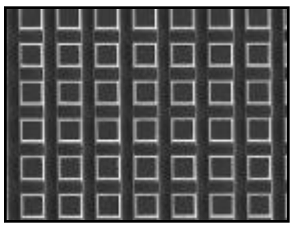
Other surfaces:
PDMS CoP: 25.3 ± 15.3
Vs.
Glass: 9.8 ± 13.6 (p = 0.028)
(Glass II: 7.1 ± 5.8)

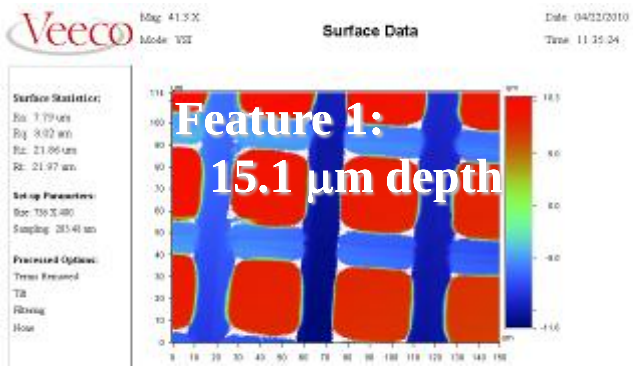
Gastropod surface selection: aestivation on screen pattern

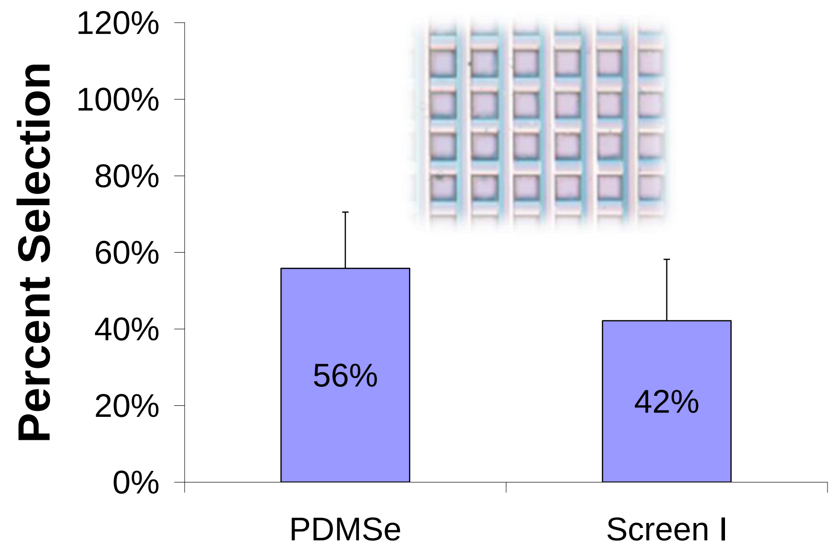
Snails can sense surfaces and change mucus properties:



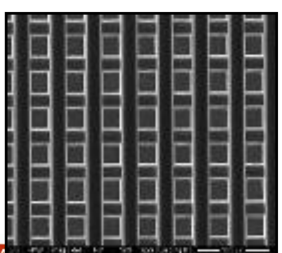
- **25 μm Screen I**

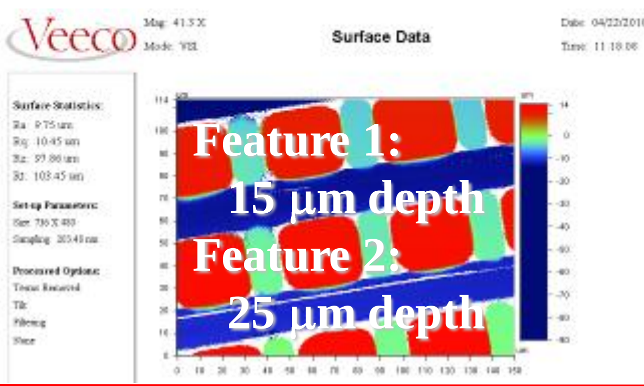


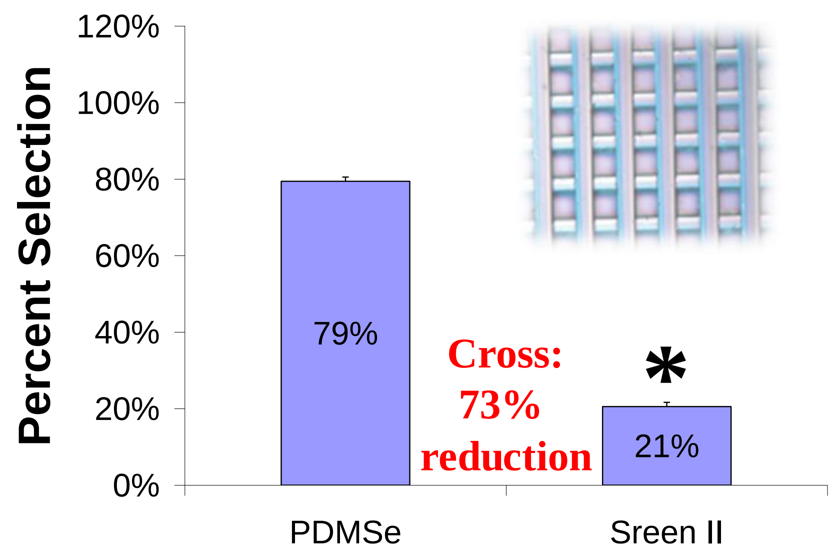




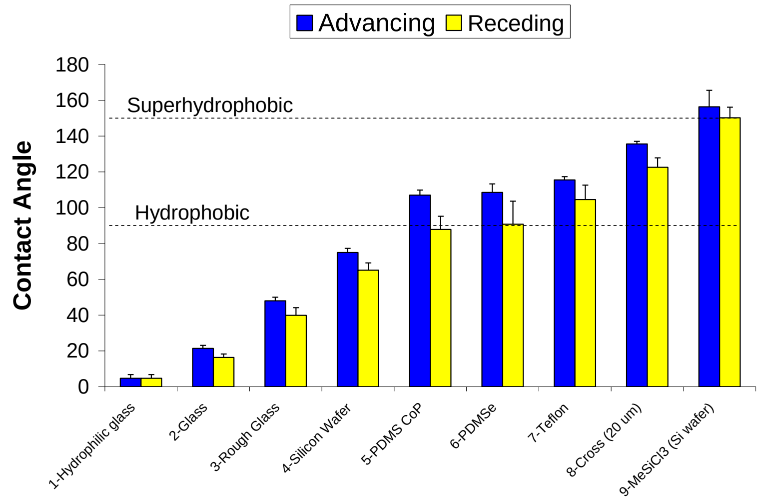
- **25 μm Screen II**

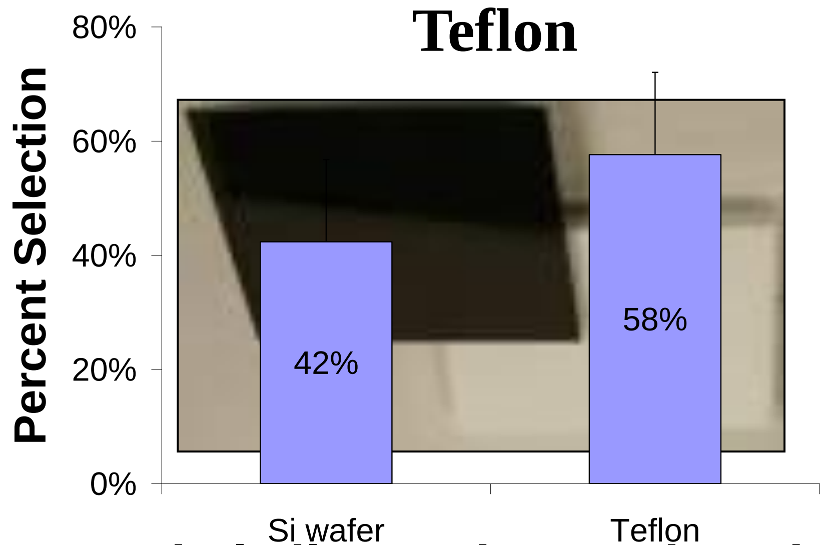


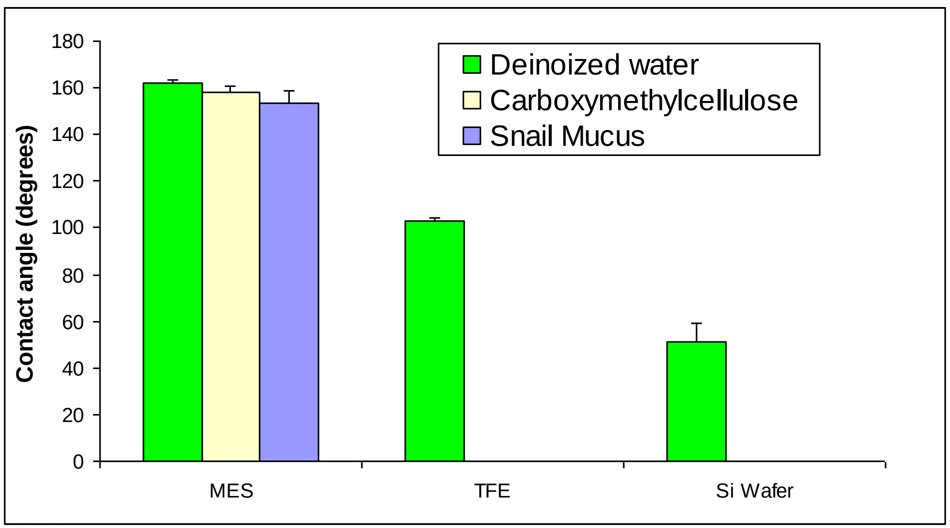




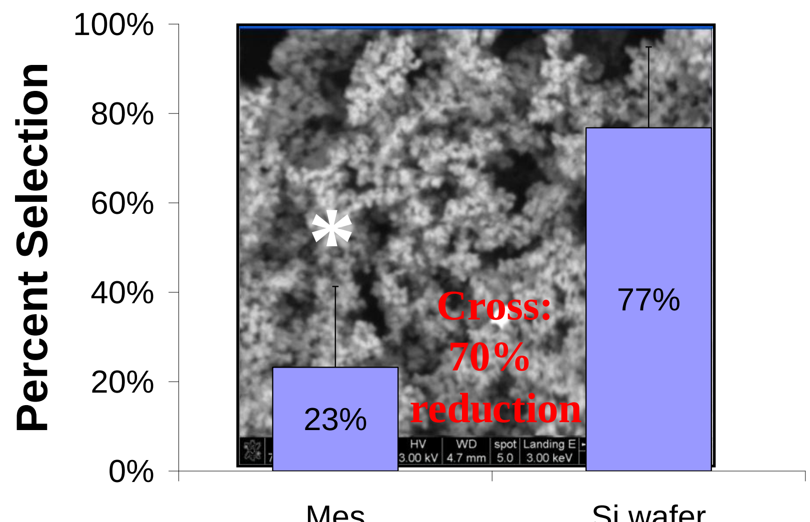
Gastropod surface selection: aestivation on hydrophobic surfaces



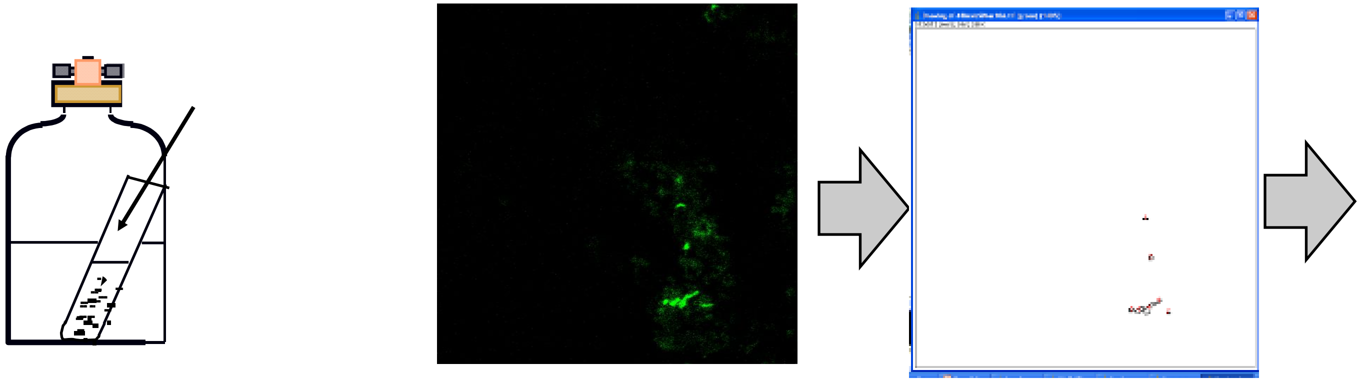




- **Methyl silsesquioxane (MES)**

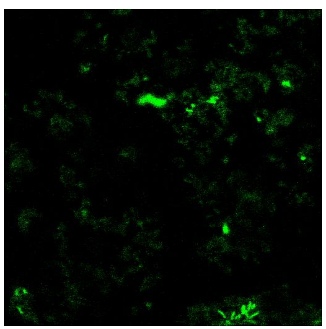


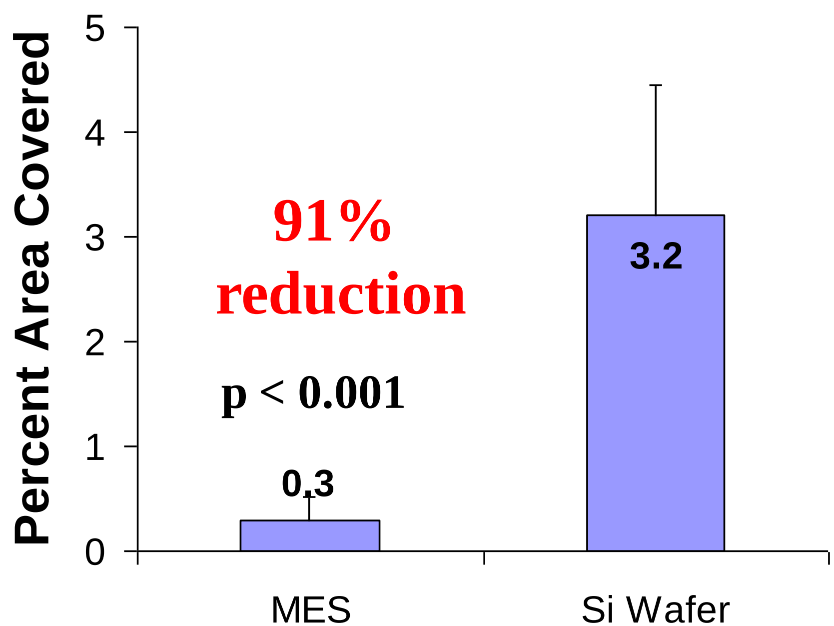
Biofilm bioadhesion: *MES xerogel*



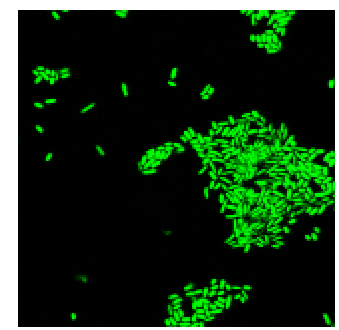
0.1% of total area covered

MES



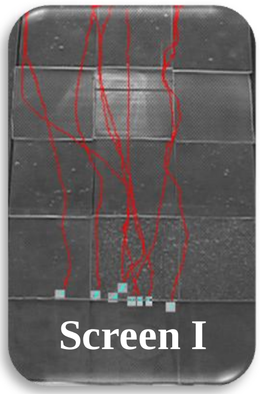


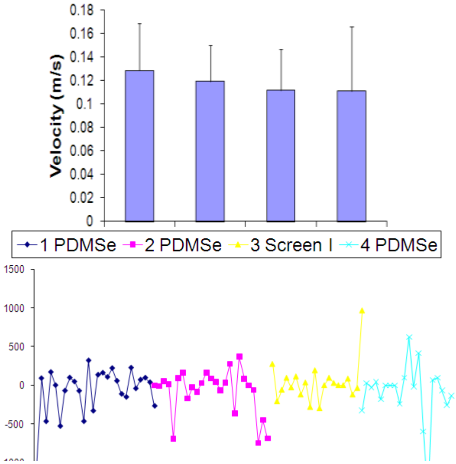
Si Wafer



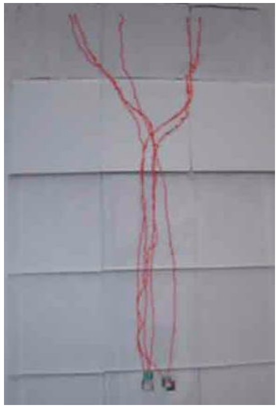
Gastropod real-time behavior at surface interface

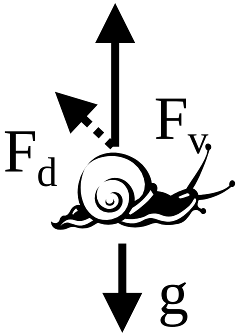
- **No effect (7)**



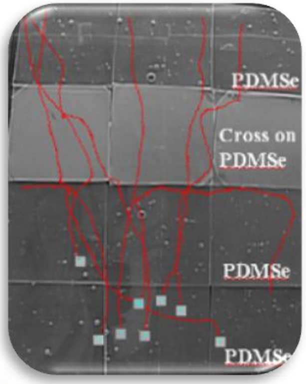


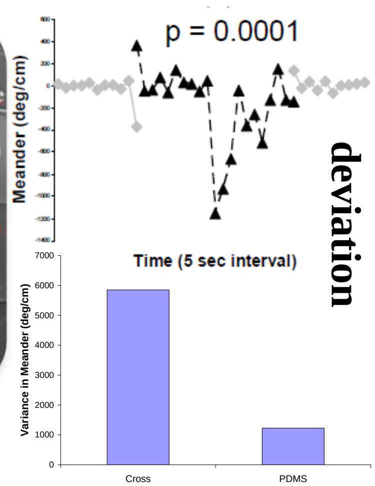
- **Teflon vs. glass**



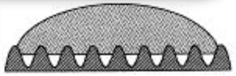


- **Cross vs. PDMSe**

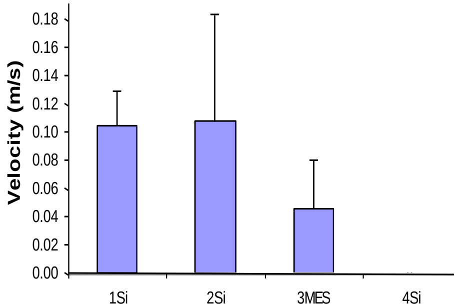




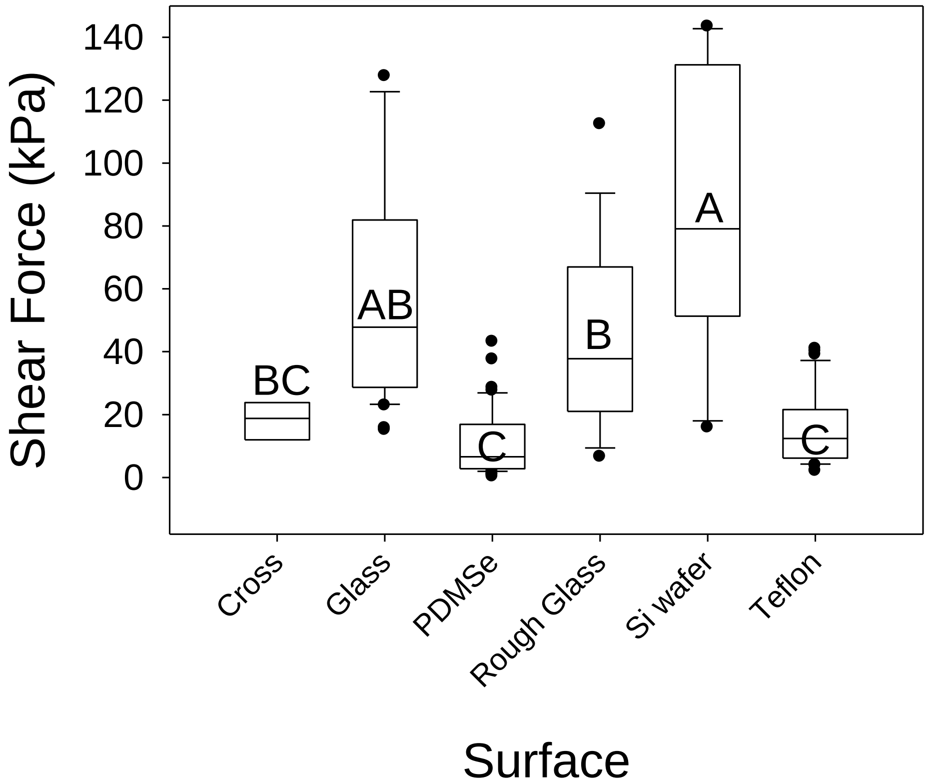
75% behavior deviation



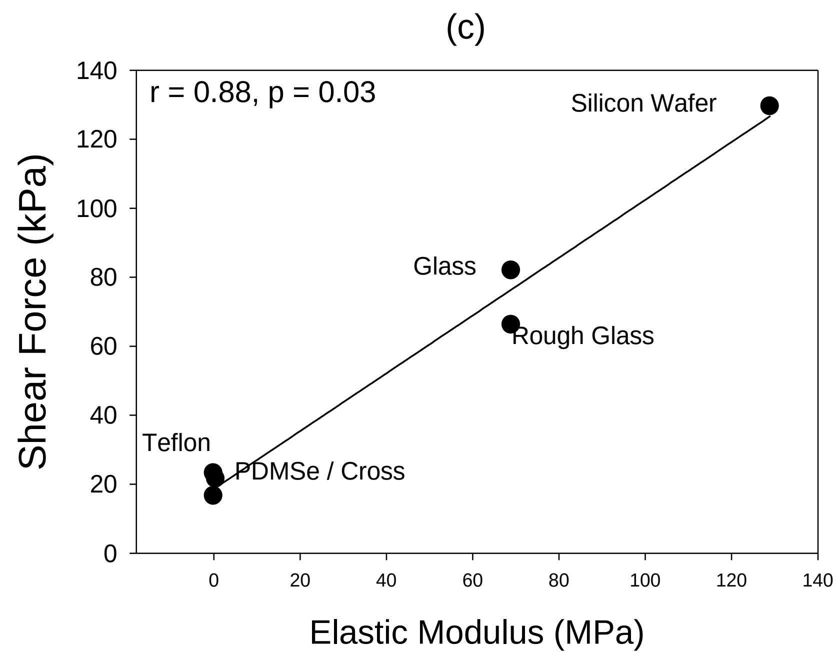
- **MES vs. Si wafer**



Gastropod bioadhesion strength: shear force for removal



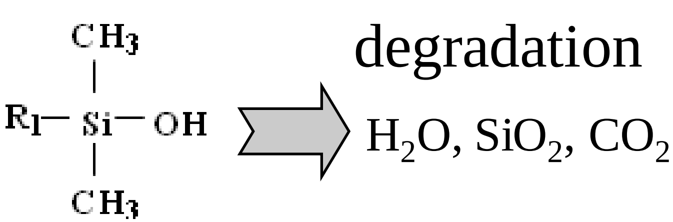
75th percentile



$$\text{Adhesion Strength } (\tau) = \frac{F(\text{in N})}{A(\text{in m}^2)}$$

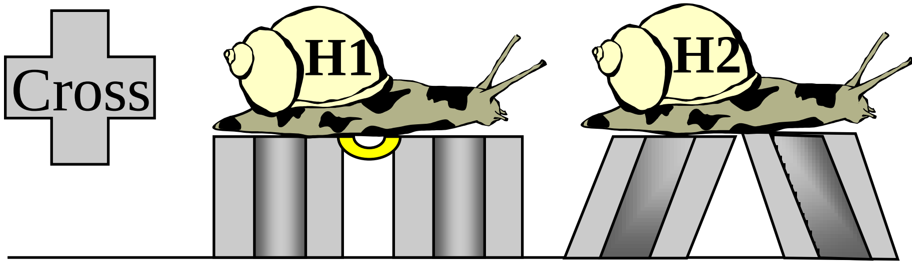
Conclusions

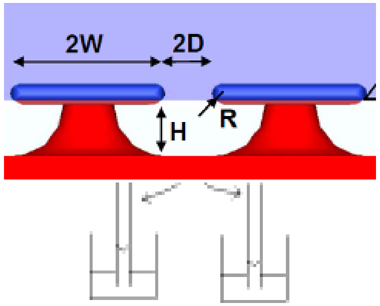
- Surface roughness controls behavior
  - Non-patterned roughness facilitates gastropod selection preference
  - Cross pattern tessellation reduces gastropod selection preference
  - 20 µm feature magnitude superior to 3 and 60 µm
- Material elastic modulus controls bioadhesion strength
  - Low modulus materials reduce shear adherence
  - High modulus materials increase shear adherence
- Cross tessellation on PDMSe provides
  - Behavioral deterrence for aestivation
  - Mechanical property to reduce adhesion strength for ease of removal
- Triethylsilanol
  - Initially toxic
  - Breaks down rapidly, nontoxic

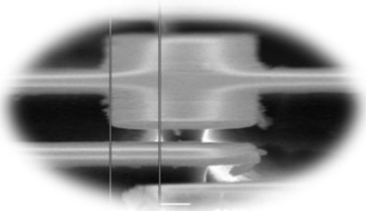


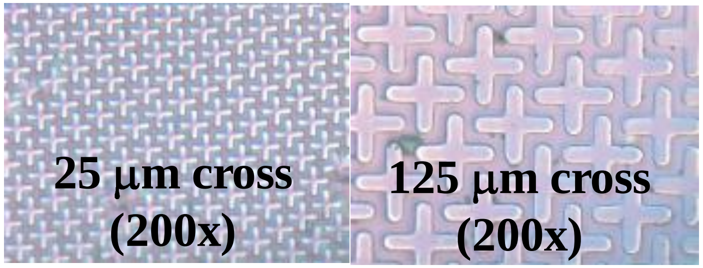
Future Research

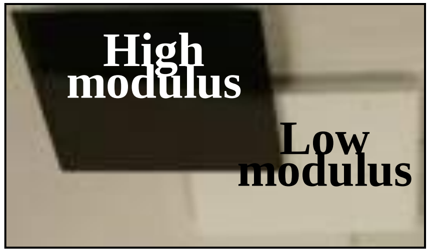
- Why successful?
  1. H1: Mucus breakthrough pressure
  2. H2: Feature modulus
- Silanized Micro hoo doo
  - Tuteja et al, Science, 2007
  - High breakthrough pressure (> 1400 Pa)
- Different sizes (25, 125 μm) and 25 μm cross spacings (4, 10 μm)
- Cross: PDMSe vs. Si wafer











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